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The Sigma Team for Minor Actinide Separation (STMAS) was formed within the USDOE Fuel Cycle Research and Development (FCRD) program in order to develop more efficient methods for the separation of americium and other minor actinides (MA) from used nuclear fuel. The development of processes for MA separations is driven by the potential benefits; reduced long-term radiotoxicity of waste placed in a geologic repository, reduced timeframe of waste storage, reduced repository heat load, the possibility of increased repository capacity, and increased utilization of energy potential of used nuclear fuel. The research conducted within the STMAS framework is focused upon the realization of significant simplifications to aqueous recycle processes proposed for MA separations. This report describes the research efforts focused upon the identification of a process suitable diluent for a flowsheet concept for the separation of MA which is based upon the dithiophosphinic acid (DPAH) extractants previously developed at the Idaho National Laboratory (INL).

Research conducted at the INL has demonstrated the use of a synergistic mixture of bis(3,5-bis(trifluoromethyl)phenyl) dithiophosphinic acid (DPAH “0”) and trioctylphosphine oxide (TOPO) for the selective separation of minor actinides from the lanthanides.¹ A separation factor of $^{Am}S_{Eu} = 160$ has been determined for the separation of Am(III) from Eu(III) using a solvent composition of 0.5 M “0” + 0.1 M TOPO dissolved in toluene. The aqueous phase used for this determination was a simulated dissolved fuel raffinate containing ~3 g/L lanthanides and ~3 g/L other fission products adjusted to a total acidity of 1.0 M H^+ using nitric acid. The low flash point of a solvent based upon toluene severely limits the applicability of this An/Ln separation scheme to “real-world” situations. Experiments performed during FY-13 identified a new diluent, mesitylene (1,3,5-trimethylbenzene), with a significantly higher flash point (relative to toluene). This aromatic solvent has a flash point of 53.0 °C (127.4 °F).

Flowsheet modeling (assuming a UREX-like raffinate adjusted to a total acidity of 0.75 M HNO_3) demonstrated that the targeted minor actinide separation was achievable using the proposed INL DPAH solvent composition. Even though mesitylene was able to dissolve 0.5 M “0” + 0.1 M TOPO and the results of distribution ratio measurements and preliminary batch contact flowsheet tests were very promising, concerns about the possibility of the diluent nitration and subsequent formation of unstable nitro-aromatic species has created serious reservations about the use of this organic solvent in an actual process.

In order to identify a better diluent for the INL DPAH process solvent, the solubility of DPAH “0” in the solvents listed in Table 1 were examined. Due to the limited amounts of the extractant available only the solubility of DPAH “0” at 0.5 M (and in some cases at 0.1 M) concentration in these solvents was examined. These solubility experiments were performed under ambient laboratory conditions ($T = 20 \pm 2$ °C).

The identification of a process suitable diluent has proven to be a daunting task. Of the investigated solvents, only toluene and mesitylene were able to dissolve DPAH “0” at the 0.5 M concentration. DPAH “0” initially dissolved at 0.5 M using either *t*-butylbenzene, cyclohexanone, or 1,3-diethylbenzene as the diluent. However after standing overnight, significant precipitate formation was noted for the *t*-butylbenzene and 1,3-diethylbenzene solvents. In addition to the precipitate formation, the

cyclohexanone solution developed a strong yellow/orange coloration. The remaining alkyl aromatic compounds and the Solvesso 150 ND (a proprietary “heavy” aromatic hydrocarbon fluid produced by ExxonMobil Chemical Company) were all unable to solubilize the DPAH at the desired concentration. Experiments performed at the INL previously demonstrated that the INL DPAH compounds were insoluble in aliphatic solvents, i.e. dodecane. The trifluoromethylphenyl sulfone (FS-13) solvent is routinely used at the INL to prepare 0.1 M solutions of various INL DPAH derivatives. While higher concentrations (up to 0.5 M) solutions are possible for the bis(*o*-trifluoromethylphenyl) dithiophosphinic acid dissolved in trifluoromethylphenyl sulfone (FS-13), the DPAH “0” is not soluble in FS-13 above approximately 0.2 M.

Table 1. Flashpoint of investigated solvents.

Solvent	Flashpoint (°F)	Flashpoint (°C)
Toluene	39	4
<i>t</i> -Butylbenzene	93	34
Cyclohexanone	111	44
1,3-Diethylbenzene	124	51
sec-Butyl benzene	126	52
Mesitylene	127	53
<i>t</i> -Butyltoluene	129	54
Solvesso 150 ND	145	63
Isopentyl benzene	149	65
Pentyl benzene	151	66
1,4-Disopropylbenzene	169	76
1,3-Disopropylbenzene	171	77
Dodecane	181	83
FS-13	252	122

The difficulty of dissolving DPAH “0” solvents other than toluene or mesitylene is attributed to the large molecular of DPAH “0” relative to other INL DPAH compounds. Calculated values of the molecular volume of several DPAH compounds² are listed in Table 2. Even though the data listed in Table 2 represent, at best, internally consistent estimates, the molecular volume of DPAH “0” is approximately 30% larger than the other INL DPAH derivatives.

Table 2. Calculated estimates of the molecular volume of several DPAH compounds.

Compound	Estimated molecular volume, Å ³
bis(3,5-bis(trifluoromethyl)phenyl) dithiophosphinic acid	287
bis(<i>o</i> -trifluoromethylphenyl) dithiophosphinic acid	230
<i>o</i> -trifluoromethylphenyl, <i>m</i> -trifluoromethylphenyl dithiophosphinic acid	228
bis(<i>m</i> -trifluoromethylphenyl) dithiophosphinic acid	224
bis(<i>p</i> -trifluoromethylphenyl) dithiophosphinic acid	223

Recently, the selective separation of actinides (U, Np, Pu, Am, and Cm) from simulated dissolved fuel raffinate with a total acid concentration of 0.5 M HNO₃ was accomplished using a solvent comprised of 0.5 M bis(*o*-trifluoromethylphenyl) dithiophosphinic acid + 0.1 M TOPO dissolved in FS-13.³ In addition, Freiderich and co-workers demonstrated that hydrazine protected several DPAH compounds (including bis(*o*-trifluoromethylphenyl) dithiophosphinic acid and bis(3,5-bis(trifluoromethyl)phenyl) dithiophosphinic acid) from degradation when toluene solutions were contacted with 2 M HNO₃ for up to two months. Based upon these results, further experiments related to the application of INL DPAH extractants to An/Ln separations will be performed using FS-13.

References

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